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Blue Electroluminescent Devices Based on Soluble Poly(p-pyridine)

by

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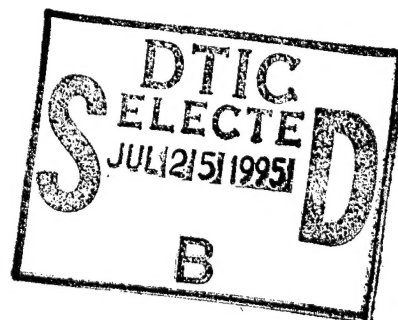
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Blue electroluminescent devices based on soluble poly(*p*-pyridine)

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Abstract

We have fabricated unilayer electroluminescent devices from soluble poly(*p*-pyridine) (PPy). The solubility of PPy in weak acids allows direct spin casting of the polymer films. The electroluminescence (EL) spectrum peaks at 2.5 eV (497 nm) corresponding to white light weighted towards the blue end of the spectrum. The photoluminescence (PL) spectrum peaks at 2.35 eV (530 nm). The operating voltages of the devices ranged from 4 to 12 V with current densities of 6 to 8 mA/mm². We compare our devices with similar blue emitting devices based on poly(*p*-phenylene) (PPP).

Electroluminescent devices utilizing conjugated polymers as emitting layers have become a subject of great interest since the first report of electroluminescence (EL) in poly(*p*-phenylene vinylene) (PPV) in 1990 [1]. Conjugated polymer devices promise advantages over traditional semiconductor devices in processibility and in applications such as large area displays [2]. Since their initial fabrication many improvements in the devices have been made including: (1) emission across the entire visible spectrum [3,4] (2) low drive voltages [5] and (3) good efficiency and brightness [2]. Unlike inorganic light-emitting diodes (LEDs), conjugated polymer LEDs are readily available in all three primary colors [1,3,6–9].

We have fabricated blue light-emitting diodes using poly(*p*-pyridine) (PPy) as the emitting layer. Conjugated polymers that luminesce with blue wavelengths are generally difficult to produce because most conjugated polymers have band gaps too small to allow blue emission [10]. Consequently, copolymers, blends, or partially conjugated polymers have been used [2,7,11–18]. An easily synthesized conjugated homopolymer is extremely desirable for fundamental studies. To date the only conjugated polymer candidates are poly(alkylfluorenes) [8,19] and polyparaphenylene (PPP) [6,20]. As a blue emitter PPy potentially offers advantages over PPP and poly(alkylfluorenes). Processing is simpler because the PPy itself is soluble in hydrochloric or formic acid, allowing spin casting directly from solution. Direct spin casting avoids the use of precursor routes and subsequent thermal conversion necessary when using other common polymer emitters [1,6]. Unlike other conjugated polymers PPy contains a nitrogen heteroatom; therefore, the emission spectrum of PPy can be tuned via quaternization (including protonation) of the nitrogen site. By adding a charged species to the nitrogen site, we can manipulate the electronic structure and thereby the emission wavelength. In addition, PPy has high thermal stability and shows no thermal degradation below 270°C [21]. Moreover, PPy is electron deficient (as compared to PPP), making it more resistant to oxidation.

The chemical structure of PPy is shown in the inset of Fig. 1b. PPy was synthesized by a reductive-metal-mediated coupling polymerization [22]. This process was effected by tetrakis(triphenylphosphine) nickel which was prepared *in situ* from reduction of NiCl₂ by

Zn in the presence of triphenylphosphine and DMF solvent. The addition of an equal molar amount of 2,5-dibromopyridine to this mixture at 50°C resulted in the formation of PPy as a yellow precipitate. The precipitates were repeatedly washed and dried under vacuum. The resulting PPy is soluble in formic and hydrochloric acid [22].

The light-emitting devices consist of an emitting layer sandwiched in between two thin electrodes. Transparent indium-tin oxide (ITO) is used as the anode and a low work function metal such as Al is used as the cathode. The emitting layer consists of a spin-coated film of PPy with an active area of 2 mm².

The ITO coated glass was obtained from Delta Technologies, Ltd (CG-60IN-S209) and had a resistance of less than 20 Ω/\square . The ITO was cleaned using techniques suggested in Ref.16 in order to keep the drive voltage as low as possible. The PPy film was spun-cast at 2000 rpm from a 10 mg/mL solution of formic acid under ambient conditions. The solution and spun films have a slight yellow color. The Al electrodes were prepared by conventional vacuum vapor deposition at pressures below 4×10^{-6} torr. Typical deposition rates ranged from 1-2 Å/s. Additionally, the substrate was water cooled during the deposition to prevent any damage due to heating. We have also fabricated devices with electrically conducting polyaniline (emeraldine salt polymer protonic acid doped with camphor sulfonic acid) (PANI) coated on the ITO as the anode.

The absorbance was measured using a Perkin-Elmer Lambda 19 UV/Vis/NIR spectrometer. The EL and PL were measured using a SPEX Fluorolog Fluorometer. The current-voltage characteristics were measured using two Keithley 195A digital multimeters. The voltage was applied with a Hewlett-Packard 6218A dc power supply.

The current-voltage characteristics of a typical device are shown in Fig. 1a. The devices show operating voltages from 4 to 12 V at current densities of 6 to 8 mA/mm². Figure 1a plots the I-V characteristics of an ITO/PPy/Al device with an ~8 Volt turn-on and an ITO/PANI/PPy/Al device with a ~4 Volt turn-on. PANI earlier was shown to decrease the turn-on voltage of PPV devices [23]. The inset of Fig. 1a shows the brightness versus voltage of the ITO/PPy/Al device and shows that the light turns on at approximately the

same voltage as the current begins to rapidly increase. Figure 1b is a logarithmic plot of the current density versus voltage for an ITO/PPy/Al device and an ITO/PANI/PPy/Al device. At low voltages (below the turn-on voltage) both devices have power law behavior ($I \sim V^n$) with $n < 2$. The ITO/PPy/Al device shown has an exponent $n \sim 1.8$ and the ITO/PANI/PPy/Al device shown has an exponent $n \sim 1.1$. The higher absolute current density for the ITO/PANI/PPy/Al device suggests the transport from the ITO/PANI into the emitter occurs more readily than from the ITO directly into the emitter. Above the turn-on voltage both devices show higher power law behavior ($n \sim 4.7$ and $n \sim 3.9$ for these ITO/PPy/Al and ITO/PANI/PPy/Al devices respectively), which varies somewhat with device fabrication.

Figure 2 shows the absorption and PL spectra of a PPy film and the EL spectrum of a typical ITO/PPy/Al device. The PL spectrum was excited at 3.36 eV (370 nm). The peak of the PL is apparently Stokes shifted by 1.0 eV with respect to the peak absorption to 2.35 eV (530 nm) and is devoid of vibronic structure in contrast to other electroluminescent polymers such as PPV and MEH-PPV [2,4]. The PL spectra of PPP and PPy are qualitatively the same with a slight peak energy shift from 2.5 eV (PPP) [6] to 2.35 eV (PPy). The strong fluorescence of PPy indicates that the π band dispersion makes the singlet $\pi \rightarrow \pi^*$ state lower in energy than the singlet $n \rightarrow \pi^*$ state. This is not the case in pyridine and bipyridine which show only weak luminescence indicating the $n \rightarrow \pi^*$ state is lower in energy [24,25].

The EL spectrum was measured at 12 V and has a peak at 2.5 eV (497 nm). While the peak of the EL is in the blue-green region, the spectral breadth of the emission may allow filtering of the light output to give a blue LED. Also, the PL of PPy in solution and powder forms peaks at energies above 2.7 eV, well into the blue region suggesting that the emission from PPy films may be weighted more strongly in the blue region by changing the film preparation and morphology. It is noted that the strong redshift of emission reported for PPP derivatives [20] can be reduced by the introduction of disorder into the polymer [9]. The EL peak of PPy films is blue shifted slightly (2.35 to 2.5 eV) and broadened compared to the PL of the films. A blue-shifting and broadening of the PL of the PPy films is observed

under high-energy excitation (> 4.2 eV), possibly due to a "hot exciton" effect [25]. Such an effect may also be responsible for the difference between PL and EL in our samples. The EL is clearly visible in a dimly lit room. Methods to improve the efficiency and further blue shift the EL are under study.

In summary, we have fabricated EL devices with polypyridine as the emitting layer. Low operating voltages are attainable through the use of a layer of polyaniline between the ITO and PPy. The EL and PL spectra are peaked in the blue-green region. The simplicity of synthesis, the ability to cast PPy directly from solution and the ability to quaternize the nitrogen site make PPy potentially of interest for technological applications.

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FIGURES

FIG. 1. (a) Current-voltage characteristics for ITO/PPy/Al (\circ) and ITO/PANI/PPy/Al (\diamond) devices. The inset shows the brightness versus voltage for the ITO/PPy/Al device. (b) Log-log plot of current-voltage characteristics for ITO/PPy/Al (\circ) and ITO/PANI/PPy/Al (\diamond) devices. The lines represent fits above and below the turn-on voltages.

FIG. 2. Normalized (a) absorption, (b) photoluminescence (PL) and (c) electroluminescence (EL) of PPy spin-coated on ITO. The PL spectrum was taken with 3.4 eV excitation.

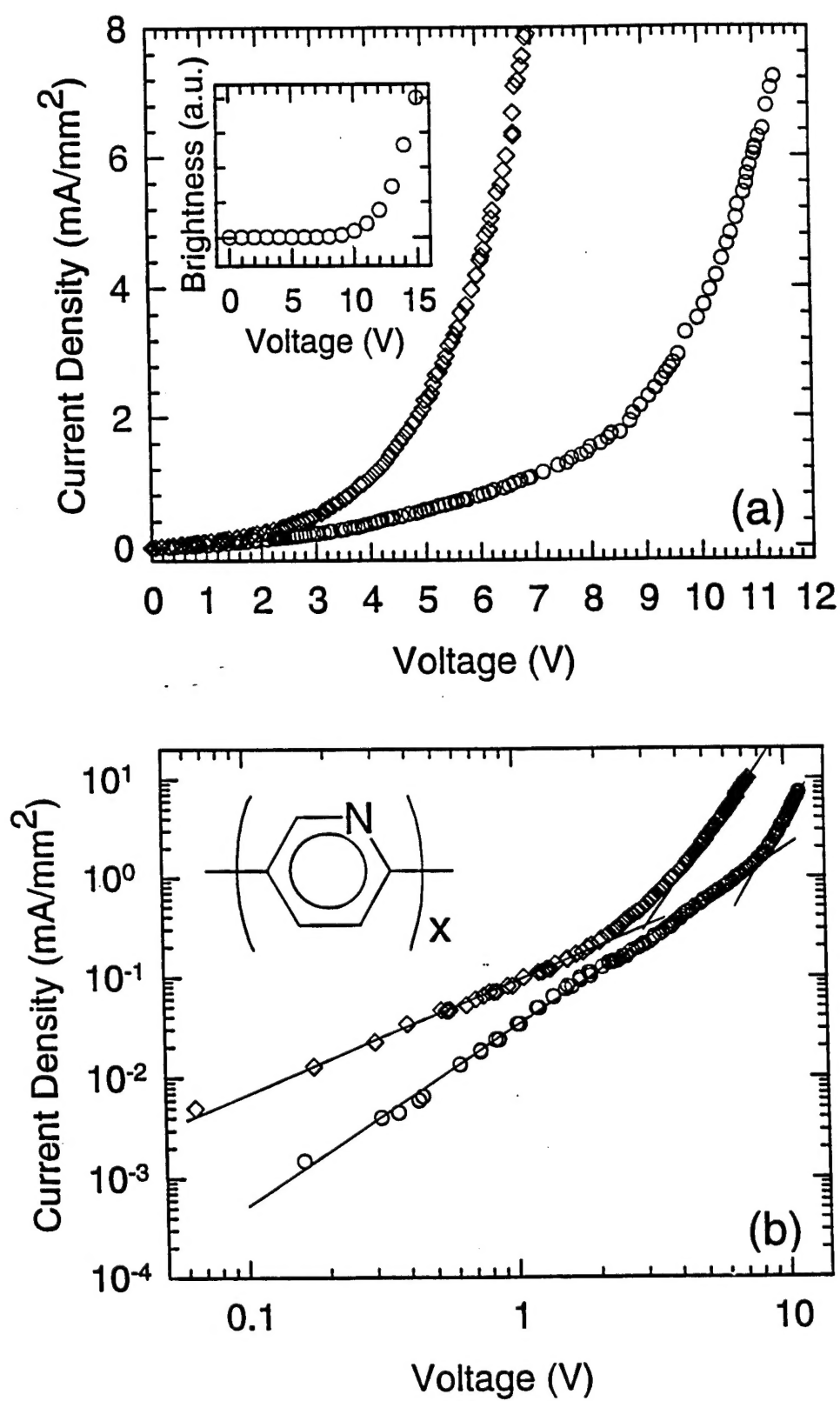
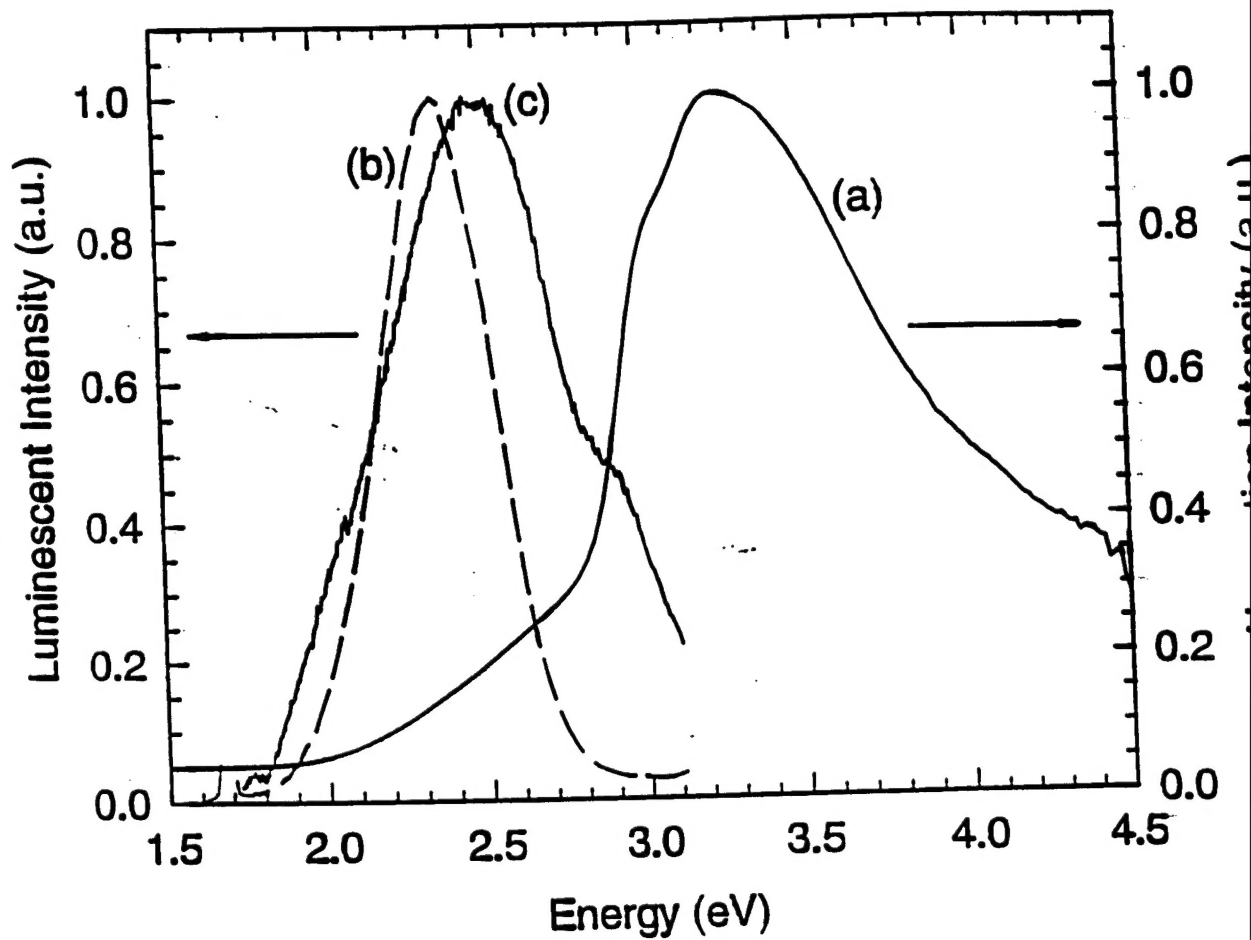


Figure 1 Gebler *et al.*



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Figure 2